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6. AUTHOR(S)

S. Esayan, J.I. Scheinbeim and B.A. Newman

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Polymer Electroprocessing Laboratory
Department of Chemical and Biochemical Engineering
College of Engineering, Rutgers University
P.O. Box 909
Piscataway, NJ 08855-0909

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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Dr. Kenneth J. Wynne
Office of Naval Research
Arlington, VA 22217-5660

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Polymer Electroprocessing Laboratory
Department of Chemical and Biochemical Engineering
College of Engineering
Rutgers University
Piscataway, NJ 08855-0909

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S. Esayan, J.I. Scheinbeim and B.A. Newman
Department of Mechanics and Materials Science
Rutgers University
Piscataway, NJ 08855-0909

Abstract

The temperature and frequency dependences of the pyroelectric current have been studied in Nylon 7 and Nylon 11 ferroelectric polymer films. A remarkable change of value of the pyroelectric currents near the glassy transition temperature (T_g) was observed.

Analyses of experimental data show that the temperature behavior of pyroelectric currents can be explained by the competition of the primary and secondary effects. Currents due to these effects have different signs. Below T_g, the dominant component of the pyroelectric current is primary pyroelectricity, and above T_g the secondary effect becomes dominant. Mechanisms producing pyroelectric currents in Nylon 7 and Nylon 11 are discussed.

Most studies of pyroelectric behavior in polymers have been directed to the first known class of ferroelectric polymers, polyvinylidene fluoride and its copolymers. However, melt-quenched and cold-drawn odd-numbered nylons (nylon 11, 9, 7, 5) are also ferroelectric and large piezoelectric coefficients have been measured for these polymers[1]. Preliminary investigations of the pyroelectric properties of nylon 11 were also carried out by Litt et al[2]. In this work, the behavior of pyroelectric currents in nylon 11 and nylon 7 films were studied extensively in order to understand the origin of pyroelectricity in the odd-numbered nylons.

Nylon films (thickness ~20-30μ) were prepared by melting nylon powder between aluminum foils in a hot press at ~200°C, and pressing into thin films which were then quenched into an ice-water bath. These films were then uniaxially cold-drawn at room temperature to a draw ratio 3:1. To measure the pyroelectric current, gold electrodes (thickness ~400°Å, area $\approx 30 mm^2$) were deposited on opposite sides of the films. Samples were poled at room temperature by applying a triangular-shaped electric field with a maximum amplitude of 200 MV/m and a time period ~600 seconds with the sample immersed in a silicon oil bath. The capacitance of the films was ~10 pF.

A dynamic technique was used to study the pyroelectric properties of the resulting films. To create a sinusoidal temperature variation, a modulated light beam from a He-Ne laser (633nm, 1mW) was focused on the electrodes. The periodic currents were measured with a lock-in amplifier with 10^7-$10^8 \Omega$ input impedance.

The major advantages of this technique are higher sensitivity and that it allows one to measure only the current generated at the chopping frequency. Additionally, the method can be used to measure the currents both in-phase and out of phase with the modulated beam.

Samples were supported, but unconstrained, in a thermostated cell with an optical window. Typically, heating (cooling) rates of 1°C/min were used for measurements. The temperature of the sample was monitored with a copper-constantan thermocouple. The

emf from the thermocouple was recorded as the abscissa on an X-Y recorder with the voltage from the lock-in amplifier as ordinate.

In dielectric materials, currents which are induced by changes in temperature, T, can be written as[3]:

$$i_T = RT + P_y A \frac{dT}{dt} \qquad (1)$$

where R is constant, A is the electrode area, and $\frac{dT}{dt}$ is the time derivative of the temperature, T.

$$P_y = \frac{\partial P_s}{\partial T} + \alpha_i c_{ik} d_{ik} \qquad (2)$$

is the pyroelectric coefficient, where P_s is the spontaneous polarization, α_i, c_{ik} and d_{ik} are the coefficient of thermal expansion, elastic modulus and piezoelectric coefficients, respectively.

The first term in equation (2) represents primary pyroelectricity and the second term describes the secondary pyroelectric effects. Complex piezoelectric and elastic behavior $\left(d_{ik} = d^R_{ik} - i d^I_{ik}, \ c_{ik} = c^R_{ik} - i c^I_{ik} \right)$ has been observed for many polymers including the odd-numbered nylons[4]. Therefore, the secondary pyroelectric current has a real component with pyroelectric coefficient, P^R, 90° out of phase with the temperature wave (modulated beam) and an imaginary component with coefficient, P^I, 180° behind the phase of the laser beam:

$$P_y = P_y^R - i P_y^I, \left(i = \sqrt{-1} \right)$$

$$P_y^R = \frac{\partial P_s}{\partial T} + \alpha_i \left(c^R_{ik} d^R_{ik} - c^I_{ik} d^I_{ik} \right) \qquad (3)$$

$$P_y^I = \alpha_i \left(c^R_{ik} d^I_{ik} + c^I_{ik} d^R_{ik} \right)$$

For nylon 11 and nylon 7 $c^I_{ik} < c^R_{ik}$ and $d^I_{ik} < d^R_{ik}$[4], so the contribution of $\alpha_i c^I_{ik} d^I_{ik}$ term in P_y^R can be neglected. In these dynamic measurements, the temperature may be expressed as:

$$T = T_o + T \sin ft \qquad (4)$$

The total ac current from the sample under the heating conditions presented by equation (4) can be written as:

$$i_{ac} = \left(RT - P_y^I AfT\right) \sin ft + P_y^R ATf \cos ft \qquad (5)$$

From equation (5), it follows that the ac components of the nonpyroelectric currents and the imaginary component of the pyroelectric current (i_I) are in phase with the temperature waves, whereas the ac components of the real component of pyroelectric currents (i_R) precede the temperature waves (the laser beam) by 90°. Therefore, if we measure the phase of the currents with respect to the modulated laser beam, the real component of pyroelectric current and nonpyroelectric components of the ac current can be separated. It is important to point out here that the phase between the modulated laser beam and the pyroelectric current varies with frequency near the thermal relaxation frequency[5] $f_T = \dfrac{1}{\tau_T}$, where $\tau_T = \dfrac{C\rho}{2\alpha_x} \cdot \ell \approx 0.15 \dfrac{\ell}{\mu m} \approx 1s$ is the thermal time constant, α_x is the heat transfer coefficient into air, C is the specific heat, ρ the density and ℓ is the film's thickness.

In this study, the frequencies used were in the range 5 to 150 Hz and the condition $f \gg \dfrac{1}{2\pi\tau_T}$ is satisfied, so that the phase shift between incident light and the real component of pyroelectric current is about 90° and changes very little at the frequencies utilized.

The absolute value of the pyroelectric coefficient for nylon 11 and nylon 7 was measured using a polarized PVF_2 polymer film as a reference. As the experiments show, the values of the pyroelectric coefficients depend strongly on sample preparation conditions (oriented or unoriented, annealing temperature) and the relative humidity of the environment. At room temperature and at ~30% relative humidity, we obtain the following ratios: $\dfrac{\left(P_y^R\right) nylon 11}{\left(P_y^R\right) PVF_2} = 0.57 \pm 0.1$ and $\dfrac{\left(P_y^R\right) nylon 7}{\left(P_y^R\right) nylon 11} = 1.4 \pm 0.2$ when

measurements are carried out at $f = 98Hz$. The pyroelectric currents in phase and out of phase with the laser beam were measured as a function of temperature $(T = 290 - 420K)$ and frequency $(f = 5 - 150Hz)$.

Fig. 1 shows the measured currents for nylon 7 as a function of frequency. As shown in Fig. 1(a), the real part of the current decreases until the frequency reaches the $10 - 20Hz$ region, when the current changes its sign. The imaginary part of the current decreases continuously with increasing frequency. Upon switching the polarization of the films, Fig. 1(b) shows that both currents change sign as expected. It is important to note that the magnitude of the switching currents decreased. The value of the frequency of modulation, f_o, where the currents change their signs depends on sample preparation conditions and temperature. The same type of behavior was also observed for nylon 11.

As for the temperature dependencies of the pyroelectric currents, they have a different behavior for the imaginary (180° out of phase with the temperature wave) and for the real (90° out of phase with the temperature wave) components. The temperature dependencies of the pyroelectric currents also are different for the real components at measurement frequencies $f < f_o$ and $f > f_o$. The temperature dependence of the imaginary components of current showed a small broad maximum near T_g. The temperature dependence of the real components of current was studied in more detail, because it consists of only a pyroelectric contribution according to eqs. 3 and 5. The results of these experiments are presented in Figs. 2 and 3.

Fig. 1 shows that there are two contributions to the real component of the pyroelectric currents and that they have opposite signs. At frequencies $f > f_o$, the dominant contribution to pyroelectricity most likely comes from space change mechanisms[6]. It is well known that pyroelectric currents due to space charge and molecular dipoles have different signs. At low frequencies the space charge contribution should tend to zero and molecular dipole mechanism is dominant at low frequency, therefore, the sign of the total pyroelectric current may change with frequencies.

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The frequency dependence of the imaginary component has a simpler character. This current decreases with increasing modulation frequency (more complicated dependence than $1/f$). We suggest that both the i_I and the low frequency part of the real component of current are connected to the same relaxation process in the glassy state. The switching of signs of the currents after switching of the polarization direction shows that they are connected with the polar state of the films. One of the possible mechanisms of these currents which is typical for polymers can be the change of depolarization field at the boundary between crystalline and amorphous regions with changing temperature. As for decreasing of the pyroelectric current at switching, it is reasonable to assume that the effect is due to decreasing of the switching component of remanent polarization during annealing of samples[7].

The temperature dependence of i_R measured at frequencies $f > f_o$, (Figs. 2 and 3) according to equation 3 is closely related to that of the real component of the piezoelectric coefficient, elastic constants and thermal expansion. These coefficients have strong temperature dependence near $T = T_g$[4]. There was no significant change with temperature for T below T_g. Then, i_R decreased rapidly and changed its sign at 90-115°C (Figs. 2 and 3). It is usually the case that the primary pyroelectric effect has a remarkable temperature dependence only near to the ferroelectric phase transition region.[5]. Therefore, temperature dependences of the real part of pyroelectric currents are probably due to secondary pyroelectricity caused by a piezoelectric response to the thermal strain induced by the laser beam.

Analyses of the experimental results in Figs. 2 and 3 show that for both nylon 7 and nylon 11, the primary and secondary components have different signs. Below T_g, the piezoelectric coefficients are small, therefore, the dominant component of the pyroelectric current is primary pyroelectricity. Above T_g, the piezoelectric coefficients increase remarkably[4] and at $T \geq 100°C$ the secondary effect becomes dominant and can account for ~60% and ~70% of the observed total pyroelectricity in nylon 11 and nylon 7,

respectively. The qualitive agreement between i_R and d_{31} was satisfactory, but an absence of data for α_i, d_{33}, d_{31} and c_{ik} made quantitive comparison difficult.

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Figure Captions

Fig. 1   Current vs. frequency for the nylon 7 film poled by (a) $100 \dfrac{MV}{m}$ and (b) $-100 \dfrac{MV}{m}$ fields.

Fig. 2   Pyroelectric current (the real component) as a function of temperature for nylon 7 films.

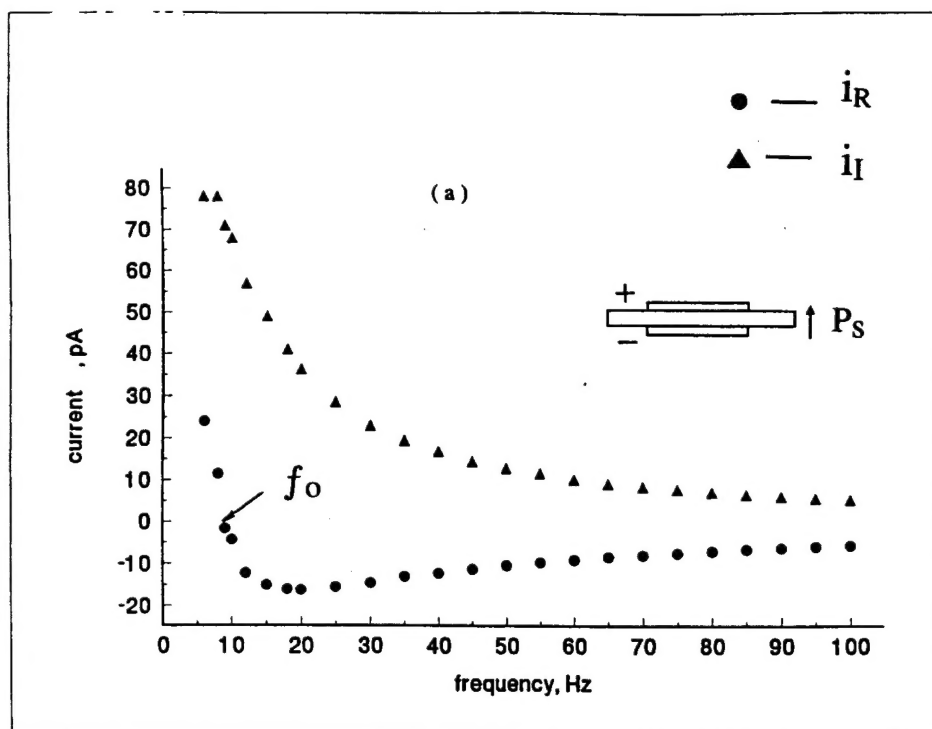Fig. 3   Pyroelectric current (the real component) as a function of temperature for nylon 11 films.

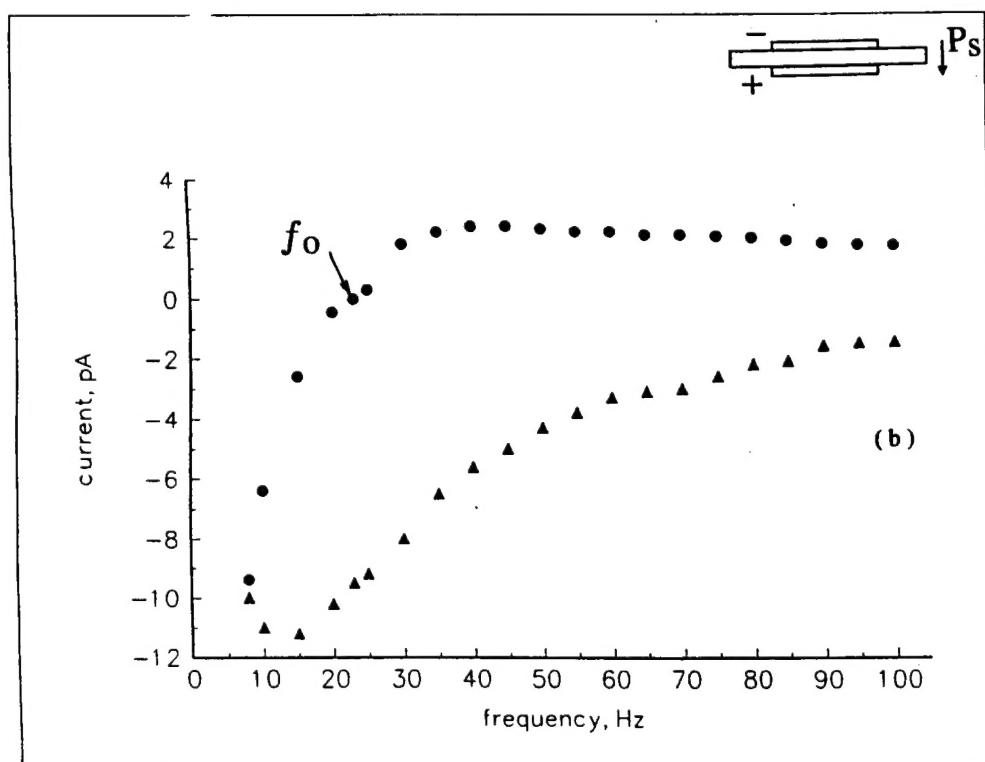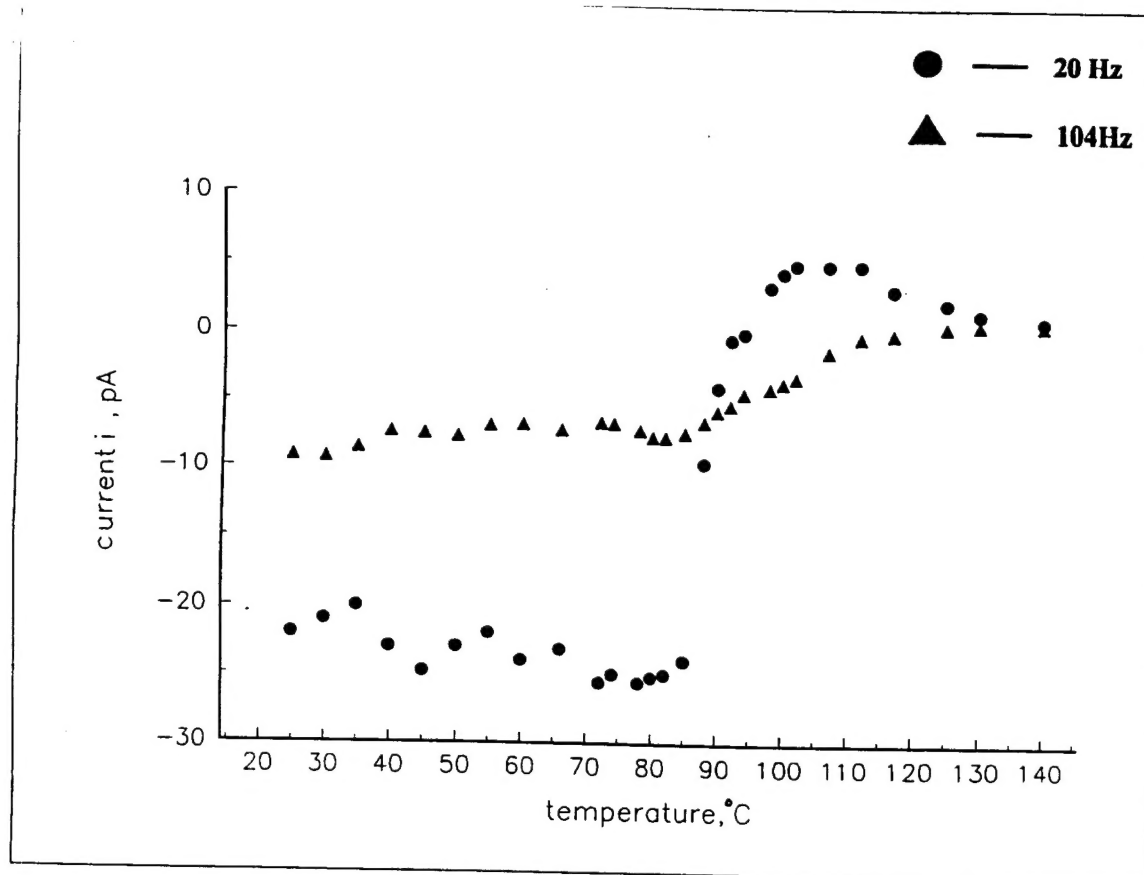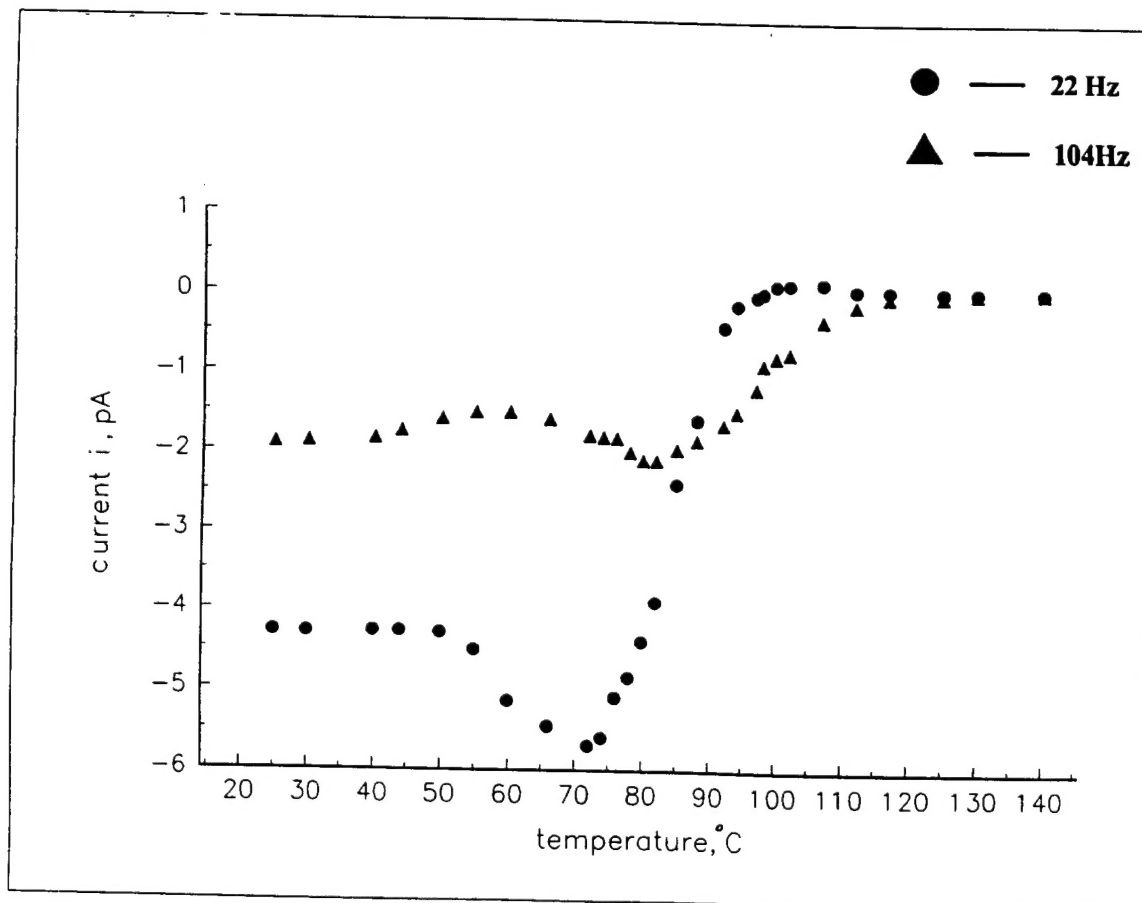Fig. 1(a)

Fig. 1(b)

Fig. 2

Fig. 3